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Method and installation for production of noble gases and oxygen by means of cryogenic air distillation

The present invention relates to a method and a plant for producing oxygen and rare gases by air distillation.

A weak krypton/xenon mixture is conventionally produced from a purge at the main vaporizer of a double air separation column (see "Tieftemperaturtechnik" by Hausen and Linde, 1985 edition, pp. 337-340 and "Separation of Gases" by Isalski, 1989 edition, pp. 96-98). The oxygen produced is then withdrawn from the low-pressure column a few stages above the vaporizer. If the oxygen is withdrawn in gaseous form, this arrangement allows a substantial fraction of the krypton present in the air and all of the xenon to be recovered.

However, in the case of a unit producing oxygen by what are called "pumped" methods, about 30% of the krypton and of the xenon present in the air are "lost" in the liquid oxygen withdrawn from the low-pressure column.

DE-A-2603505 discloses an air separation unit in which a fluid containing krypton and xenon is produced in a purification column fed with two streams of rich liquid coming from the medium-pressure column, the reboiling in the purification column being provided by a vaporizer fed with the overhead gas from an argon column.

One object of the present invention is to propose systems for increasing the krypton and xenon yield of units producing gaseous oxygen by pumping and vaporization of liquid oxygen (or more generally those with substantial withdrawal of liquid oxygen from the

bottom of the low-pressure column) and, preferably, also producing argon.

Another object of the present invention is again to have a principal vaporizer with a high oxygen content and massively purged, and thus to greatly limit the concentration of hydrocarbons/impurities (the advantage of a pumped "oxytonne"), which is not the case with the conventional scheme producing a weak mixture of krypton and xenon.

One subject of the invention is a method for producing oxygen and rare gases by distillation in a column system comprising at least one medium-pressure column, one low-pressure column and one auxiliary column, in which method:

i) at least one stream of cooled and purified air is sent to the medium-pressure column where it is separated;

ii) at least a first nitrogen-enriched stream is withdrawn from the medium-pressure column and at least one portion of this stream is sent directly or indirectly to the low-pressure column;

iii) an intermediate stream is withdrawn from an intermediate level of the medium-pressure column;

iv) a stream, enriched with oxygen relative to the intermediate stream, is withdrawn from the bottom of the medium-pressure column and sent to the bottom of the auxiliary column;

v) a nitrogen-rich stream is withdrawn from the top of the low-pressure column;

vi) an oxygen-rich liquid stream is withdrawn from the low-pressure column as product, optionally after a vaporization step in order to form a gaseous product; and

vii) an oxygen-enriched stream, which is also enriched with krypton and with xenon relative to the second oxygen-enriched stream, is withdrawn from the auxiliary column,

characterized in that the intermediate stream is sent to the low-pressure column and a liquid stream containing at least 78 mol% nitrogen is sent as reflux to the auxiliary column.

Preferably, the liquid stream sent as reflux to the auxiliary column is liquefied air and/or liquid enriched with nitrogen relative to a liquefied air stream sent to the medium-pressure column.

According to optional aspects:

- the bottom of the auxiliary column is heated by an overhead gas from an argon column;
- the liquefied air and/or the liquid enriched with nitrogen relative to the air is produced by heat exchange with the oxygen-rich liquid stream coming from the bottom of the low-pressure column, optionally after a pressurization step;
- the nitrogen-enriched liquid contains at least 80 mol% nitrogen;
- the liquefied air does not come from the medium-pressure column, the liquid stream sent to the top of the auxiliary column is richer in nitrogen than the intermediate stream; at least 10% of the oxygen produced is withdrawn in liquid form from the low-pressure column.

Another subject of the invention is a plant for producing oxygen and rare gases by distillation in a column system comprising at least one medium-pressure column, one low-pressure column and one auxiliary column, which plant comprises:

i) means for sending at least one stream of cooled and purified air to the medium-pressure column where it is separated;

ii) means for withdrawing at least a first nitrogen-enriched stream from the medium-pressure column and means for sending at least one portion of this stream directly or indirectly to the low-pressure

column;

iii) means for withdrawing a nitrogen-rich stream from the top of the low-pressure column;

iv) means for withdrawing an intermediate stream from an intermediate level of the medium-pressure column;

v) means for sending a stream, richer in oxygen than the intermediate stream, from the bottom of medium-pressure column into the bottom of the auxiliary column;

vi) means for sending a liquid stream as reflux to the auxiliary column;

vii) means for withdrawing an oxygen-rich liquid stream from the bottom of the low-pressure column as product, optionally after a vaporization step in order to form a gaseous product; and

viii) means for withdrawing a third oxygen-enriched stream, which is also enriched with krypton and with xenon relative to the second oxygen-enriched stream, from the auxiliary column,

characterized in that it includes means for sending, as reflux stream to the auxiliary column, liquefied air or a liquid stream enriched with nitrogen relative to a liquid air stream sent to the medium-pressure column.

According to other optional aspects, the plant includes:

- a purification column, means for sending the third oxygen-enriched stream into the top of the purification column and means for withdrawing a fourth oxygen-enriched stream, constituting a mixture enriched with krypton and xenon, at least a few theoretical stages lower down in the column; and

- an exchange line in which the liquefied air and/or the liquid enriched with nitrogen relative to the air is produced by heat exchange with the oxygen-rich liquid stream coming from the bottom of the low-pressure column, optionally after a pressurization step.

The invention will now be described with reference to figures 1 to 9, which are diagrams showing the principle of plants according to the invention.

In the example shown in figure 1, a double air separation column comprises a medium-pressure column K01 and a low-pressure column K02 that are thermally coupled by means of a principal vaporizer E02 that is used to condense at least part of the gaseous overhead nitrogen of the column K01 by heat exchange with oxygen from the bottom of the column K02.

An argon column K10 is fed with an argon-enriched fluid 7 coming from the low-pressure column K02 and an argon-enriched liquid 9 is returned from the argon column K10 to the low-pressure column K02. An argon-rich stream ARGON is withdrawn from the top of the column K10.

In the case of pumped units, a portion of the dry and decarbonized air is compressed in an air booster (not illustrated) up to the pressure sufficient to allow vaporization of the optionally pumped oxygen. It is then condensed in the main exchange line (not illustrated). At the cold end of the main exchange line, this flow is expanded in a valve or in a hydraulic turbine. The liquid phase LIQ AIR of this fluid can then be distributed as streams 1, 3 and 5 between the medium-pressure column K01, the low-pressure column K02 and the auxiliary column K05, respectively. The liquid contains 78 mol% nitrogen.

The other portion of the medium-pressure air MP AIR is cooled in the main exchange line and sent to the bottom of the medium-pressure column K01.

The principle of the present invention is to concentrate the krypton and the xenon in a rich liquid RL2, which will then be treated in an auxiliary column

K05.

Two rich liquids RL1 and RL2 are therefore withdrawn from the medium-pressure column K01, namely a "conventional" rich liquid withdrawn from an intermediate level a few stages above the bottom of the column and containing a small quantity of krypton and of xenon, RL1, and a rich bottoms liquid concentrated with krypton and xenon, RL2. This "conventional" rich liquid RL1 can then be sent to the column K02 after having been subcooled.

The rich bottoms liquid RL2 is sent to the K10 argon mixture condenser E10 after subcooling (not illustrated). Stages are installed above this equipment in order to concentrate the krypton and the xenon at the argon mixture condenser. This assembly constitutes the column K05. A portion of the reflux from this column is provided by a portion 5 of the liquid air LIQ AIR not feeding the column K01, after this has been subcooled. The other portion of the reflux is provided by a portion 15 of the mean liquid 11 conventionally sent to the column K02 via the line 13 and containing at least 80 mol% nitrogen. A gas 16 is withdrawn from the intermediate level of the column K05 below the points of reflux injection, and constitutes the vaporized rich liquid. It is then recycled in the column K02. The overhead gas WN2' from the column K05 constitutes a portion of the waste gas WN2 leaving the cold box.

The purge PURGE from the mixture condenser E10 contains most of the krypton and xenon that are present in the air and have been treated by the columns K01 and K05. This flow feeds a device for concentrating the rare gases. For example, it may be sent into the weak krypton/xenon mixture column (K90). The bottom of this column contains the product to be beneficiated. The vapor 17 coming from the column K90 is sent back into

the bottom of the column K05.

The column K90 is heated by a stream of air forming a fraction of the MP AIR. The liquefied air thus formed may be sent back to the medium-pressure column K01 and/or to the low-pressure column K02.

The production of liquid oxygen LO is withdrawn as bottoms from the column K02, level with the principal vaporizer E02. Unlike the conventional scheme for krypton and xenon production, the principal vaporizer is therefore massively purged.

The liquid oxygen LO is preferably pressurized by a pump and then vaporized in the exchange line or in a dedicated vaporizer, by heat exchange with the pressurized air. Alternatively, a nitrogen cycle may serve to vaporize the liquid oxygen LO.

In the following figures, various alternative embodiments deriving from figure 1 will be presented. The elements common with figure 1 will not be described a second time.

In the case of figure 2, all of the liquid air LIQ AIR coming from the main exchange line is sent into the column K01. An intermediate fluid in liquid form 1′ is withdrawn from the column K01 (preferably at the level where the liquid air is introduced or at a level above this level). Next, after having been subcooled, it is distributed between the column K02 and the column K05 as two streams 3 and 5. Stream 11 containing at least 80 mol% nitrogen is sent to the top of the column K05.

In the case of figure 3, based on figure 1, one top section of the column K05 has been removed. The reflux from this column is provided only by liquid air 5, preferably subcooled. This liquid air is produced by vaporization of the liquid oxygen LO pumped and

vaporized in the exchange line. All the lean liquid 13 is sent to the low-pressure column K02.

In addition, all of the liquid air LIQ AIR present at the outlet of the exchange line can be withdrawn from the column K01 (preferably at the point of introduction of the liquid air) and then distributed between the column K02 and the column K05 after having been subcooled, as shown in figure 4.

In the case of figures 5 and 6, based on figures 3 and 4, the waste gas WN2' from the column K05 is sent back into the column K02 below the point of injection of the lean liquid 13.

In the case of figure 7, based on figure 5, the stream 16 is omitted and replaced with a stream of waste nitrogen WN2' sent from the top of the auxiliary column K05 to an intermediate point on the low-pressure column.

In all the figures described above (figures 1 to 7), it is possible to couple the plant with the conventional scheme for producing krypton and xenon. To do this, it is necessary to install stages for enrichment of the bottom in the column K02. The liquid oxygen LO is produced a few stages above the principal vaporizer E02. A purge 21 is withdrawn level with the principal vaporizer E02. It contains about 70 mol% krypton and all of the xenon present in the column K02. It is sent to the column K90 in order to recover the rare gases.

An example is given in figure 8.

In all the above figures (figures 1 to 8), the coproduction of argon is mentioned. However, it is possible to fit the plants described above to a unit that does not produce argon. For example, it is sufficient to install an exchanger for condensing a

fraction of the gas 7 withdrawn from the column K02. Once liquefied, it is sent (9) into the column K02. This thus provides the reboiling in the column K05.

An example is given in figure 9.

In the case of a scheme with a blowing turbine, the blown air is sent into the bottom of the column K05 so as to recover the krypton and xenon that it contains.

In addition, the schemes illustrated in figures 1 to 9 may also include distillation assemblies, such as for example an Etienne column (a column that operates at an intermediate pressure between the medium and low pressures and fed with rich liquid). In this case, it is possible to modify the top condenser of an Etienne column, by replacing the argon column K10 of figures 1 to 9 with an Etienne column according to the same principle: addition of stages above the condenser in order to concentrate the rare gases.

It is perhaps also advantageous not to send all of the liquid air into the top of the auxiliary column but to introduce, at this inlet of the column, only a stream that ensures an L/V (the ratio of the falling liquid flow rate to the rising gas flow rate in the distillation section) needed to concentrate the Kr and Xe in the bottom of K05, thereby limiting the oxygen concentration in the bottom of K05. The remainder of the liquid air stream is then sent, with the rich liquid RL2, into the bottom of the auxiliary column.